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A STUDY OF ARSENICAL DUSTING OF CABBAGE IN RELATION TO POISON RESIDUES

By CHAS. E. SMITH, *associate entomologist*, and W. J. REID, JR., P. K. HARRISON, and C. O. BARE, *assistant entomologists, Division of Truck Crop and Garden Insect Investigations, Bureau of Entomology and Plant Quarantine* [1]

The Bureau of Entomology and Plant Quarantine in Cooperation with the Louisiana and South Carolina Agricultural Experiment Stations

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INTRODUCTION

During the cabbage-growing seasons of 1932–33 and 1933–34 a series of experiments was conducted at the field laboratories of the Bureau of Entomology and Plant Quarantine at Charleston, S. C., and Baton Rouge, La., to determine the relation of the number of applications at specified rates and strengths of the arsenicals commonly applied on cabbage for the control of leaf-feeding insects and the stage in the development of the crop when the applications are discontinued, to the quantity of residue present at the time of harvest on the portion of the plants usually marketed.

Six experiments were conducted at each place, involving one experiment for each of the six cabbage-growing seasons during the 3-year period. This provided an opportunity to study the influence of varying climatic conditions, especially rainfall and temperature, upon the quantity of poison residue remaining on the cabbage after various intervals between the application of the insecticide and harvest of the cabbage. Each experiment covered a series of plots for each material and dilution used. In the majority of the experiments the plots were one-twentieth of an acre in area with rows 3 feet apart; the number of rows per plot ranged from three to eight, six rows being used in the majority of the experiments.

[1] Acknowledgments are due W. A. Thomas for general supervision of the Charleston studies and L. B. Reed for his assistance. The analytical work in connection with the Charleston experiments was performed by C. R. Gross of the Division of Insecticide Investigations of this Bureau. At Baton Rouge, the residue determinations for one experiment were made by Sylvan B. Falck under the supervision of E. C. Boudreaux of the New Orleans office of the Food and Drug Administration of the U. S. Department of Agriculture. The analyses for the remainder of the experiments were made by J. L. Farr and W. P. Denson, assistant chemists, under the supervision of A. P. Kerr, chief chemist of the Louisiana Agricultural Experiment Station. The writers gratefully acknowledge their indebtedness for these important contributions to the work.

METHODS

Essentially the same methods were employed in all the experiments. In each experiment the dust mixtures were applied to several plots. By dropping one plot each time the applications were made, a series of plots was obtained which had received applications varying by one successively from the minimum to the maximum number. Undusted plots were provided as checks in all of the experiments.

MATERIALS TESTED

At Charleston, in experiments 1 to 4 (season 1932–33), paris green and lime (1 to 10) and lead arsenate and lime (1 to 5) were used. The desired rates per acre per application were 16.5 pounds of the paris green-lime mixture and 24 pounds of the lead arsenate-lime mixture, and these were approximated quite closely. In experiments 5 and 6 (season 1933–34) paris green and lime (1 to 9) and undiluted calcium arsenate were used. The desired rate per acre per application of each was 20 pounds, and this was approximated quite closely.

At Baton Rouge, in experiments 1 to 3 (season 1932–33), paris green and lime (1 to 10) and calcium arsenate and lime (1 to 5) were used. The rates per acre per application applied in these experiments ranged from approximately 10 pounds of the dust mixtures on the plots receiving the minimum number of applications, which were made when the plants were small, to approximately 20 pounds in the later applications on the plots receiving the maximum number. During the season of 1933–34, in experiments 4 and 5, mixtures of paris green and lime and calcium arsenate and lime, each containing 10 percent and 5 percent of arsenic trioxide, respectively, or the equivalent, were used. The dust mixtures were applied at the rates of 10 pounds of the 10-percent and 20 pounds of the 5-percent mixture per acre per application. In experiment 6, paris green and lime (1 to 9) and undiluted calcium arsenate were used and applied at the rate of approximately 15 pounds per acre per application.

Hydrated builders' lime was used in all of the mixtures given above. The analyses of the arsenicals employed are given in table 1.

TABLE 1.—*Analyses of arsenical materials used in experimental dusting of cabbage at Charleston, S. C., and Baton Rouge, La.*

Constituents or properties	Paris green			
	At Charleston		At Baton Rouge	
	Experiments 1 to 4	Experiments 5 and 6	Experiments 1 and 2	Experiments 3 to 6
	Percent	*Percent*	*Percent*	*Percent*
Moisture	0.4	0.66	0.52	0.46
Arsenious oxide (As_2O_3)	57.1	56.76	55.38	57.50
Arsenic oxide (As_2O_5)	.23	.38	.54	.69
Copper oxide (CuO)	30.7	30.98	32.01	31.23
Water-soluble As_2O_3	.66	1.04	1.34	.87

TABLE 1.—*Analyses of arsenical materials used in experimental dusting of cabbage at Charleston, S. C., and Baton Rouge, La.*—Continued

Constituents or properties	Lead arsenate,[1] at Charleston, experiments 1 to 4	Calcium arsenate	
		At Charleston, experiments 5 and 6	At Baton Rouge, experiments 1 to 6
	Percent	*Percent*	*Percent*
Moisture	0.2	1.61	1.10
Arsenic oxide	32.2	38.95	41.94
Arsenious oxide	.0	.25	.12
Water-soluble As_2O_5	.16	.11	.10
Lead oxide	64.00		
Calcium oxide		44.47	47.28
Loss on ignition		8.69	5.89

[1] Hypothetical composition: Dilead arsenate, $PbHAsO_4$, 92.7 percent; trilead arsenate, $Pb_3(AsO_4)_2$, 6 percent.

The dusts were applied with rotary-type hand dusters by passing over the row once when the plants were small, and twice at an angle on each side, after the plants began to head. The applications for each experiment were made at equal intervals unless weather or other conditions interfered.

In the Charleston experiments, the Charleston Wakefield variety of cabbage was used exclusively. At Baton Rouge, the Copenhagen Market variety was used in all of the experiments except nos. 3 and 5. The Charleston Wakefield was used in experiment 3 and Stein Flat Dutch in experiment 5.

SAMPLING AND RESIDUE DETERMINATIONS

The samples consisted of 10 heads taken at random from each experiment, except for Charleston experiments 1 and 2, in which they consisted of 20 plants. The plants were trimmed to conform to United States grade No. 1 (allowing four loose wrapper leaves), except in Charleston experiment 1, in which the entire plants, except the stalk below the bottom leaves, were analyzed.

The arsenical residues were determined by following the method recommended by the Association of Official Agricultural Chemists.

In addition to the regular residue determinations, two special analytical studies were made on samples of cabbage submitted from the Charleston laboratory. The objective of these studies was twofold: (1) The determination of the number of cabbage plants required for a reliable sample for arsenical-residue determination, and (2) the determination of the normal arsenical content of untreated cabbage grown in the Charleston area, and whether this was due to soil contamination externally or to root absorption and normal plant metabolism.

In the first study it was found that an error as high as 20 percent of the mean would permit a proper interpretation of the data and that a sample of approximately 10 heads would be sufficient. In the second study it was found that untreated cabbage grown in the Charleston area normally contains approximately 0.0008 grain of arsenic trioxide per pound in the compact inside leaves, and approximately 0.0017 grain in the outside loose leaves, one-third of the latter resulting from external contamination.

At the beginning of this study it was realized that the growth habit of cabbage heads (i. e., from within, accompanied by the progressive loosening of some of the outer leaves) is an important factor in determining when the application of poisonous insecticides should be discontinued in order that the harvested product may not contain an excess of harmful residue. Hence 25 plants in each experiment were marked at the time the last application of dust was made, by cutting a V-shaped notch in the youngest exposed leaf and recording the position of the marked leaf at the time of sampling.

The data obtained from these notching tests demonstrate that Copenhagen Market cabbage grown at Baton Rouge and marketed as U. S. grade No. 1 may include, late in the fall, some of the leaves that become visible 30 days before maturity, and, in the spring, under favorable growing conditions, some of the leaves that become visible 10 to 15 days before maturity. The corresponding periods of time for the Charleston Wakefield variety grown at Charleston were longer and ranged from 20 to 40 days, depending upon the character of the season.

RESULTS

The pertinent data obtained in experiment 1 at Charleston are given in table 2.

TABLE 2.—*Arsenic residue* [1] *on the loose leaves, stripped heads, and entire plants of 20-plant samples of Charleston Wakefield cabbage that were dusted with paris green and lime (1 to 10) and lead arsenate and lime (1 to 5), experiment 1, Charleston, S. C.*

From last dusting to sampling			Total applications	Paris green and lime, 1 to 10				Lead arsenate and lime, 1 to 5			
Period	Duration of period	Rainfall		Average applications per acre	Residue As_2O_3 per pound plant material			Average applications per acre	Residue As_2O_3 per pound plant material		
					Loose leaves	Stripped head	Whole plant		Loose leaves	Stripped head	Whole plant
	Days	*Inches*	*Number*	*Pounds*	*Grain*	*Grain*	*Grain*	*Pounds*	*Grain*	*Grain*	*Grain*
Dec. 5–Dec. 15	10	0.44	7	20.4	1.260	**0.028**	0.3694	25.5	0.560	**0.033**	0.2274
Nov. 25–Dec. 15	20	.95	6	19.6	.322	**.011**	.1101	25.4	.307	.009	.1073
Nov. 15–Dec. 15	30	1.89	5	19.4	.175	.005	.0572	25.5	.100	.003	.0432
Nov. 5–Dec. 15	40	2.82	4	16.5	.056	.002	.0202	24.0	.145	.003	.0461
Oct. 25–Dec. 15	51	4.99	3	16.5	.012	.004	.0074	24.0	.013	.002	.0057
Oct. 14–Dec. 15	62	7.30	2	16.5	.016	.002	.0067	24.0	.007	.003	.0042
Oct. 5–Dec. 15	71	8.50	1	16.5	.006	.001	.0026	24.0	.020	.005	.0096

[1] Treatments leaving a residue exceeding the legal tolerance of 0.01 grain of arsenic trioxide per pound of marketable product are shown in bold-faced type.

These data show that a large portion of the arsenic residue on cabbage treated with paris green or lead arsenate is found on the loose leaves. The legal tolerance of 0.01 grain of arsenic trioxide per pound was exceeded on the entire plant when dusted four times, the last application being made 40 days before harvest, under weather conditions which included 2.82 inches of rainfall. It was exceeded on the stripped heads, in the instance of paris green, when the last of six applications was made 20 days before harvest and the precipitation for the period totaled 0.95 inch.

The results of experiments 2 to 6 at Charleston and of experiments 1 to 6 at Baton Rouge are given in tables 3 and 4, respectively.

TABLE 3.—*Arsenic residue* [1] *on cabbage dusted with different quantities, dilutions, and numbers of applications of paris green, lead arsenate, and calcium arsenate, experiments 2 to 6, Charleston, S. C.*

From last dusting to sampling			Total applications	Residue of As_2O_3 per pound of marketable cabbage			
				Paris green and lime		Lead arsenate and lime, parts by weight, 1 to 5	Calcium arsenate, undiluted
Period	Duration of period	Rainfall		Parts by weight, 1 to 10	Parts by weight, 1 to 9		
Experiment 2:	*Days*	*Inches*	*Number*	*Grain*	*Grain*	*Grain*	*Grain*
Dec. 23–Jan. 2	10	0.06	8	**0.0790**		**0.0460**	
Dec. 14–Jan. 2	19	.51	7	**.0160**		**.0190**	
Dec. 3–Jan. 2	30	.80	6	.0100		.0070	
Nov. 23–Jan. 2	40	1.31	5	.0030		.0060	
Nov. 12–Jan. 2	51	2.25	4	.0020		.0020	
Nov. 2–Jan. 2	61	3.18	3	.0010		.0040	
Oct. 20–Jan. 2	74	5.35	2	.0010		.0020	
Oct. 8–Jan. 2	86	7.66	1	.0020		.0020	
Experiment 3:							
Mar. 16–Mar. 30	14	.33	7	**.0261**		**.0103**	
Mar. 2–Mar. 30	28	1.22	6	.0021		.0017	
Feb. 16–Mar. 30	42	2.53	5	.0012		.0010	
Feb. 2–Mar. 30	56	6.95	4	.0007		.0006	
Jan. 19–Mar. 30	70	8.84	3	.0010		.0010	
Jan. 5–Mar. 30	84	11.26	2	.0007		.0007	
Dec. 22–Mar. 30	98	11.32	1	.0008		.0012	
Experiment 4:							
Apr. 20–Apr. 30	10	1.14	10	**.0162**		**.0110**	
Apr. 10–Apr. 30	20	1.76	9	.0042		.0060	
Mar. 31–Apr. 30	30	2.47	8	.0021		.0010	
Mar. 23–Apr. 30	38	2.47	7	.0004		.0006	
Mar. 13–Apr. 30	48	2.80	6	.0004		.0005	
Mar. 3–Apr. 30	58	3.69	5	.0004		.0004	
Feb. 22–Apr. 30	67	3.69	4	.0004		.0004	
Feb. 13–Apr. 30	76	5.00	3	.0004		.0004	
Jan. 31–Apr. 30	89	9.73	2	.0004		.0004	
Jan. 20–Apr. 30	100	11.31	1	.0004		.0005	
Experiment 5:							
Jan. 3–Jan. 13	10	.30	7		**0.0430**		**0.3680**
Dec. 23–Jan. 13	21	.84	6		**.0120**		**.0740**
Dec. 14–Jan. 13	30	.87	5		.0070		**.0400**
Dec. 4–Jan. 13	40	1.34	4		.0030		.0070
Nov. 24–Jan. 13	50	1.46	3		.0030		.0040
Nov. 15–Jan. 13	59	1.60	2		.0020		.0030
Nov. 4–Jan. 13	70	2.28	1		.0010		.0020
Checks: Jan. 13 [2]			0		.0020		.0020
Experiment 6:							
May 1–May 11	10	.01	8		**.1580**		**.5950**
Apr. 21–May 11	20	.08	7		**.0280**		**.0120**
Apr. 11–May 11	30	1.33	6		.0011		.0041
Mar. 31–May 11	41	1.98	5		.0009		.0015
Mar. 22–May 11	50	2.29	4		.0026		.0018
Mar. 12–May 11	60	2.49	3		.0015		.0047
Mar. 2–May 11	70	3.22	2		.0006		.0009
Feb. 20–May 11	80	3.94	1		.0004		.0003
Checks: May 11 [2]			0		.0011		.0006

[1] Treatments leaving a residue exceeding the legal tolerance of 0.01 grain of arsenic trioxide per pound of marketable product are shown in bold-faced type.
[2] Date of sampling.

DISCUSSION

According to the data presented in tables 3 and 4, Charleston Wakefield cabbage grown in the Charleston, S. C., area retained residues exceeding the legal tolerance of 0.01 grain of arsenic trioxide per pound of marketable product when dusted with paris green and lime (1 to 10) and with lead arsenate and lime (1 to 5) as many as

19 days previous to harvest, and when dusted with undiluted calcium arsenate 30 days before harvest. At Baton Rouge, on the Copenhagen Market and Charleston Wakefield varieties, the legal tolerance was exceeded on plants dusted with all dilutions of paris green used and with calcium arsenate and lime (1 to 5) 8 to 10 days previous to

TABLE 4.—*Arsenic residue*[1] *on cabbage dusted with different quantities, dilutions, and numbers of applications of paris green and calcium arsenate, Baton Rouge, La.*

From last dusting to sampling			Total applications	Residue of As_2O_3 per pound of marketable cabbage							
				Paris green diluted with lime				Calcium arsenate diluted with lime			
Period	Duration of period	Rainfall		To contain arsenic trioxide		Parts by weight		Parts by weight		To contain As_2O_3 equivalent	
				10 per cent	5 per cent	1 to 10	1 to 9	1 to 5	Undiluted	10 per cent	5 per cent
Experiment 1:	*Days*	*Inches*	*Number*	*Grain*	*Grain*	*Grain*	*Grain*	*Grain*	*Grain*	*Grain*	*Grain*
May 5–May 15	10	0.00	7			**0.0134**		**0.0162**			
Apr. 28–May 15	17	1.22	6			.0046		.0022			
Apr. 20–May 15	25	4.26	5			.0019		.0014			
Apr. 12–May 15	33	6.39	4			.0016		.0009			
Apr. 3–May 15	42	8.63	3			.0028		.0009			
Mar. 27–May 15	49	9.10	2			.0019		.0009			
Mar. 15–May 15	61	11.09	1			.0016		.0011			
Checks						.0019		.0014			
Experiment 2:											
May 13–May 23	10	.00	6			**.0238**		**.0161**			
May 3–May 23	20	.02	5			.0029		.0040			
Apr. 25–May 23	28	2.53	4			.0022		.0019			
Apr. 17–May 23	36	4.92	3			.0013		.0020			
Apr. 7–May 23	46	6.68	2			.0013		.0020			
Mar. 29–May 23	55	9.10	1			.0015		.0041			
Checks						.0018		.0012			
Experiment 3:											
June 2–June 12	10	.35	8			**.0105**		**.0315**			
May 25–June 12	18	1.96	7			.0035		.0043			
May 15–June 12	28	1.96	6			.0019		**.0103**			
May 5–June 12	38	1.96	5			.0008		.0016			
Apr. 28–June 12	45	3.18	4			.0006		.0005			
Apr. 20–June 12	53	6.22	3			.0003		.0008			
Apr. 12–June 12	61	8.35	2			.0003		.0007			
Apr. 1–June 12	72	10.59	1			.0003		.0007			
Checks						.0003		.0003			
Experiment 4:											
Dec. 18–Dec. 26	8	.70	7	**0.0122**	**0.0117**					**0.0179**	0.0069
Dec. 8–Dec. 26	18	.70	6	.0052	.0049					.0049	.0037
Dec. 2–Dec. 26	24	1.80	5	.0015	.0025					.0022	.0010
Checks				.0014							.0003
Experiment 5:											
Feb. 20–Feb. 28	8	1.13	9	.0100	**.0135**					**.0170**	**.0203**
Feb. 13–Feb. 28	15	3.33	8	.0033	.0063					**.0108**	**.0333**
Feb. 2–Feb. 28	26	5.08	7	.0015	.0015					.0087	.0070
Checks				.0017							.0007
Experiment 6:											
Apr. 28–May 7	9	.32	4				0.0042		**0.0305**		
							.0035		**.0320**		
							.0039		**.0147**		
							.0042		**.0338**		
Apr. 20–May 7	17	.45	3				.0008		.0096		
							.0021		.0041		
							.0011		.0047		
							.0009		.0039		
Apr. 11–May 7	26	2.52	2				.0006		.0003		
							.0003		.0005		
							.0005		.0006		
							(2)		.0005		
Checks							.0003		.0003		

[1] Treatments leaving a residue exceeding the legal tolerance of 0.01 grain of arsenic trioxide per pound of marketable product are shown in bold-faced type.

[2] Trace.

harvest, and also on a sample of Charleston Wakefield cabbage which received the last application of calcium arsenate and lime (1 to 5) 28 days previous to sampling. It was exceeded on plants dusted with undiluted calcium arsenate 9 days, and on Stein Flat Dutch dusted with calcium arsenate and lime containing 10 percent and 5 percent of arsenic trioxide, respectively, 8 and 15 days previous to harvest. These data show that applications of arsenic must be discontinued before the appearance of the head or wrapper leaves that will remain attached to the head when it is harvested for market. The results of these experiments indicate that the normal arsenic content of cabbage (whole plant) under South Carolina conditions averages approximately 0.001 grain of arsenic trioxide per pound.

Several factors influence the quantity of arsenical residue remaining on cabbage treated with arsenicals. The stage of plant development at the time arsenical treatments are discontinued is probably most important in determining whether or not the harvested product will contain an excess of harmful residue. The plant-growth study in conjunction with the residue determinations demonstrated that the marketable part of cabbage retaining foliage which had been exposed to the arsenical treatments may contain residue exceeding the legal tolerance, regardless of the period of time elapsing between the last application and harvesting. Normally all cabbage treated after the heads start forming (fig. 1) are included in this category.

The quantity and character of rainfall are probably second in importance. These studies show that heavy rainfall will remove a large quantity of the deposits on dusted cabbage, but ordinarily not enough to prevent the tolerance limit from being exceeded.

In addition, the season of the year when the plants are grown may affect the growth of the plants, with special reference to the development of leaves that may or may not be retained as a part of the marketed head.

Although records were obtained regarding the insecticidal value of the different treatments reported herein, it may be stated that in general such records were not conclusive, since some of the applications were made under conditions unfavorable for maximum insecticidal effects, and in some of the experiments the worm populations were insufficient for obtaining significant results. Throughout the study the worm population consisted principally of larvae of one or more of the following species: The cabbage looper (*Autographa brassicae* Riley), the imported cabbage worm (*Ascia rapae* L.), and the diamond-back moth (*Plutella maculipennis* Curtis).

SUMMARY AND CONCLUSIONS

Twelve experiments were conducted, six at Charleston, S. C., and six at Baton Rouge, La., during the seasons of 1932–33 and 1933–34 to determine the limitations imposed by residue on treatments with arsenicals in controlling worms on cabbage. Four dilutions (lime as diluent) of paris green and calcium arsenate and one dilution of lead arsenate were employed in two or more of the experiments. The rates per acre per application ranged from approximately 10 to 24 pounds, the number of applications of the different insecticides ranged from 0 to 10, and the periods of time from last dusting to sampling ranged from 8 to 100 days. The samples for residue determination consisted of from 10 to 20 plants taken at random from each

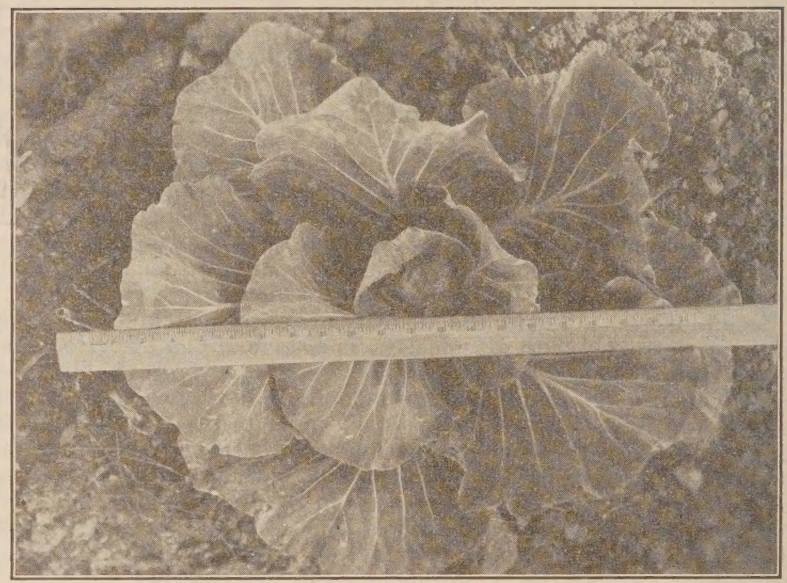

FIGURE 1.—After cabbage has reached the stage of growth shown here, arsenical treatments should not be applied, as harmful residues are likely to remain on the cabbage at harvest time.

treatment and trimmed to conform to U. S. grade No. 1—except in one experiment in which the entire leaf growth was included for analysis, the stalks being cut just below the bottom leaf. The studies were conducted under various conditions of rainfall, temperature, and soil, and with three plant varieties.

This study showed that, with intervals up to 30 days from the last arsenical application to marketing, cabbage may retain arsenical residues exceeding the legal tolerance of 0.01 grain of arsenic trioxide per pound of marketable product. The loose leaves surrounding the compact head carry the principal portion of these residues. The variety of cabbage and the quantity of rainfall also affect the residues on the harvested product. Excessive residues were found in these tests in nearly all instances where the samples were taken within 10 days after the last application of the arsenicals was made, in about 30 percent of the samples examined after about 20 days, but in less than 10 percent of the samples taken after 24 to 30 days. For periods of time exceeding 30 days no excessive residues were found during the course of these tests.

According to the data obtained in this study, it appears to be unsafe to apply arsenicals on cabbage after foliage becomes exposed which will be a part of the marketed product. In the instance of crops which will be marketed as U. S. grade No. 1, no applications should be made after the heads begin to form.

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